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Specification and Drawings, as originally filed, with Application for Patent Serial No: **2,414,622**, on December 17, 2002, by **ALBERTA RESEARCH COUNCIL INC.**, assignee of Partho Sarkar, Lorne Johanson and Hongsang Rho, for "Compact Solid Oxide Fuel Cell Stack".

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Abstract

This invention relates to a compact solid oxide fuel cell stack comprising a plurality of concentrically arranged tubular solid oxide fuel cells and end caps connecting the fuel cells. The end caps have inlets and outlets for the flow of fuel and oxidant through the stack. The arrangement of the fuel cells with in the stack define extended reactant flow paths to provide higher residence time for the reactants in the stack, thereby improving fuel conversion in an electrochemical reaction.

Attorney docket no. v80038us
document no. 86604 v1

Compact Solid Oxide Fuel Cell Stack

Field of the Invention

This invention relates generally to solid oxide fuel cells, and in particular, to a compact solid oxide fuel cell stack.

Background of the Invention

It is well known to deposit coatings of material on a conductive core by electrophoretic deposition (EPD). EPD is a combination of electrophoresis and deposition. Electrophoresis is the movement of charged particles in an electric field. Deposition is the coagulation of particles into a mass. Applicant's own PCT application no. PCT/CA01/00634 relates generally to the production of hollow ceramic membranes by EPD, and in particular to the production of hollow, tubular ceramic electrodes by EPD for solid oxide fuel cells (SOFC).

In general, a SOFC comprises two electrodes (anode and cathode) separated by a ceramic, solid-phase electrolyte. To achieve adequate ionic conductivity in such a ceramic electrolyte, the SOFC operates at an elevated temperature, typically in the order of about 1000 °C. The material in typical SOFC electrolytes is a fully dense (i.e. non-porous) yttria-stabilized zirconia (YSZ) which is an excellent conductor of negatively charged oxygen (oxide) ions at high temperatures. Typical SOFC anodes are made from a porous nickel / zirconia cermet while typical cathodes are made from magnesium doped lanthanum manganate ($LaMnO_3$), or a strontium doped lanthanum manganate (also known as lanthanum strontium manganate (LSM)). In operation, hydrogen or carbon monoxide (CO) in a fuel stream passing over the anode reacts with oxide ions conducted through the electrolyte to produce water and/or CO_2 and

electrons. The electrons pass from the anode to outside the fuel cell via an external circuit, through a load on the circuit, and back to the cathode where oxygen from an air stream receives the electrons and is converted into oxide ions which are injected into the electrolyte. The SOFC reactions that occur include:

Anode reaction: $H_2 + O^{=} \rightarrow H_2O + 2e^-$

$CO + O^{=} \rightarrow CO_2 + 2e^-$

$CH_4 + 4O^{=} \rightarrow 2H_2O + CO_2 + 8e^-$

Cathode reaction: $O_2 + 4e^- \rightarrow 2O^{=}$

Known SOFC designs include planar and tubular fuel cells. Current SOFC fuel cell stack designs typically stack the fuel cells side-by-side. For example, a tubular stack design as published by Siemens Westinghouse Power Generation features tubular fuel cells arranged in a side-by-side rectangular array. The large size of the Siemens Westinghouse fuel cells (typically > 5 mm diameter) and the relatively low power density (power output per unit volume) of the stack design makes such a fuel cell stack impractical for small scale applications such as portable electronic devices.

It is therefore desirable to provide a compact SOFC stack design that, in particular, can be made small enough with sufficient energy density for small scale applications.

Summary of the Invention

According to one aspect of the invention, there is provided a solid oxide fuel cell stack comprising a plurality of concentrically arranged tubular solid oxide fuel cells. Each fuel cell has respective anode and cathode layers sandwiching an electrolyte layer. The plurality of fuel cells include an inner fuel cell and a second fuel cell around the outside of the inner fuel cell. The inner surface of the

inner fuel cell and the outer surface of the second fuel cell both are one of the anode and cathode, and the outer surface of the inner fuel cell and the inner surface of the second fuel cell both are the other of the anode and cathode. The stack also comprises top and bottom annular end caps each having an interior perimeter and an exterior perimeter, and each connected to opposite ends of the inner fuel cell around the interior perimeter, and to opposite ends of the second fuel cell around the exterior perimeter. The end caps, outer surface of the inner fuel cell and the inner surface of the second fuel cell define an inner reactant chamber. The stack further comprises an inlet to and an outlet from the inner reactant chamber for flow of a reactant therethrough. The anode and cathodes are electrically connectable to an external circuit such that electricity is produced by electrochemically reacting fuel and oxidant reactants, wherein one reactant is fed through the inner fuel cell and over the outer surface of the second fuel cell, and the other reactant is fed through the inner reactant chamber.

The stack may further include a third tubular fuel cell that is closed at its bottom end. The third tubular fuel cell is arranged concentrically around the outside of the other fuel cells and is joined at its top end to the second fuel cell by a second annular top cap having a reactant exhaust outlet. The second annular end cap, inner surfaces of the third fuel cell, and outer surfaces of the second fuel cell form an outer reactant chamber. The inside surface of the third fuel cell is the same electrode-type as the inside surface of the inner fuel cell and the outer surface of the second fuel cell; and the outer surface of the third fuel cell is the same electrode-type as the outer surface of the inner fuel cell and the inner surface of the second fuel cell. A first reactant flow path is defined as beginning from the top of the inner fuel cell, through the inner fuel cell, into the bottom of outer reactant chamber, through the outer reactant chamber and out of the stack through the reactant exhaust outlet. A second reactant flow path is defined as through the inner reactant chamber inlet, through the inner reactant chamber and out of stack through the inner reactant chamber outlet.

Brief Description of Drawings

Figure 1 is a schematic sectioned side view of a fuel cell stack comprising multiple concentric tubular fuel cells.

Figure 2 is a schematic top plan view of the fuel cell stack of Figure 1.

Figure 3 is a schematic top plan view of a tubular fuel cell stack comprising multiple concentric tubular fuel cells and a plurality of oxidant inlets and oxidant outlets.

Figure 4 is a schematic top plan view of a tubular fuel cell stack comprising a plurality of inner tubular fuel cells surrounded by concentric middle and outer tubular fuel cells.

Figure 5 is a schematic perspective view of a fuel cell stack comprising rows of tubular fuel cells interspersed with metal sheets.

Figure 6 is a schematic perspective view of a fuel cell stack comprising a row of tubular fuel cells supported on a corrugated metal sheet.

Figure 7 is a schematic perspective view of a metal sheet in assembled form.

Figure 8 is a schematic perspective view of the metal sheet in Figure 7 in exploded form.

Figures 9 to 11 show various stages in the production of a fuel cell stack of tubular fuel cells, in which Figures 9(a) and (b) are respective side and top plan views of assembling combustible cores; Figures 10(a) and (b) are respective side and top plan views of depositing a first electrode layer on the cores; and

Figures 11(a) and (b) are respective side and top plan views of depositing an electrolyte layer on the first electrode layer.

Figure 12 is a schematic top plan view of a fuel cell stack comprising a cluster of three tubular fuel cells produced by the technique shown in Figures 9 to 11.

Detailed Description of Embodiments of the Invention

When describing the present invention, the following terms have the following meanings, unless indicated otherwise. All terms not defined herein have their common art-recognized meanings.

The term "ceramic" refers to inorganic non-metallic solid materials with a prevalent covalent or ionic bond including, but not limited to metallic oxides (such as oxides of aluminum, silicon, magnesium, zirconium, titanium, chromium, lanthanum, hafnium, yttrium and mixtures thereof) and nonoxide compounds including but not limited to carbides (such as of titanium tungsten, boron, silicon), silicides (such as molybdenum disicilicide), nitrides (such as of boron, aluminum, titanium, silicon) and borides (such as of tungsten, titanium, uranium) and mixtures thereof; spinels, titanates (such as barium titanate, lead titanate, lead zirconium titanates, strontium titanate, iron titanate), ceramic super conductors, zeolites, and ceramic solid ionic conductors (such as yittria stabilized zirconia, beta-alumina and cerates).

The term "cermet" refers to a composite material comprising a ceramic in combination with a metal, typically but not necessarily a sintered metal, and typically exhibiting a high resistance to temperature, corrosion, and abrasion.

Referring to Figure 1 and according to a first embodiment of the invention, a fuel cell stack 1 is made of three interconnected concentric tubular solid oxide fuel cells (SOFC), namely an inner fuel cell 10, a middle fuel cell 12, and an outer fuel cell 14. Each fuel cell 10, 12, 14 is a hollow tubular ceramic structure and comprises concentric membranes that serve as the anode, electrolyte, and cathode. Such fuel cells 10, 12, 14 may be of a micro-tubular type as taught in Applicant's PCT application PCT/CA01/00634. This application teaches the production of a micro-tubular SOFC by electrophoretic deposition (EPD). Tubular fuel cells produced by such a technique may have diameters as small as about 1 mm, and various cross-sectional geometries, such as circular, square, rectangular, triangular, and polygonal. Although this description primarily describes a fuel cell stack design using micro-sized tubular fuel cells with a circular cross-section, it is within the scope of the invention to use larger diameter fuel cell tubes and/or tubes with non-circular cross-sectional geometries.

In stack 1, each of the inner and outer fuel cells 10, 14 are formed so that the inner membrane layer of each tube is the anode, and the outer membrane layer is the cathode. The anode may be made of a cermet material such as Ni/ZrO_2. The middle fuel cell 12 is formed so that the inner membrane layer is the cathode, and the outer membrane layer is the anode. The fuel cells are arranged concentrically and the middle fuel cell 12 is joined to the inner fuel cell 10 at its top end by a first annular top end cap 16 and at its bottom end by an annular bottom end cap 18; the opening in the end caps 16, 18 are dimensioned to snugly fit around the periphery of the inner fuel cell 10. The middle fuel cell 12 is joined to the outer fuel cell 16 by a second annular top end cap 19; the opening in the top end cap 19 is dimensioned to snugly fit around the periphery of the middle fuel cell 12. The outer tube 14 may be formed with a closed bottom end 21, or with an open bottom end that is closed with a gas-tight bottom end cap 21. Top and bottom end caps 16, 18, 19, 21 all are connected to respective fuel cells 10, 12, 14 to form a gas-tight seal.

Instead of separate first and second top end caps 16, 19, a single annular top end cap (not shown) may be used to cap the top of the second and outer fuel cells 12, 14.

An oxidant supply conduit 20 is provided that extends from outside the fuel cell stack 1, through the first annular top end cap 16, into the annular space between the walls of the inner and middle fuel cells 10, 12 ("oxidant chamber"), and terminates near the bottom end cap 18. An oxidant exhaust outlet 22 extends from the oxidant near the top end cap 16, and through the first annular top end cap 16. Also, a fuel exhaust outlet 24 extends from the space defined by the walls of the middle and outer fuel cells 12, 14, and the bottom and top end caps 19, 21 ("fuel chamber"), through the second annular top end cap 19, and out of the fuel cell stack 1.

With the construction as described above, flow paths for fuel gas and oxidant gas are defined for the fuel cell stack 1. In particular, a fuel flow path begins at the top opening of the inner fuel cell 10 ("fuel supply inlet"), through the inside of the inner fuel cell 10, through the bottom opening of the inner fuel cell 10, and into the bottom of the fuel chamber, and finally, out of the stack 1 through the fuel exhaust outlet 24 at the top of the fuel chamber. This fuel flow path is designed to provide a long fuel path i.e., higher residence time for the fuel in the stack 1. This is expected to improve fuel conversion i.e., more fuel utilization. An oxidant flow path begins at the outside end of the oxidant supply conduit 20 ("oxidant supply inlet"), out the other end of the oxidant supply conduit 20 and into the bottom of the oxidant chamber, and upwards and out of the stack 1 via the oxidant exhaust outlet 22. The stack 1 may also be immersed in oxidant (e.g. air) so that the outer surface of the outer fuel cell 16 is exposed to oxidant.

To avoid leakage of one gas flowpath into the other, the connections establish gas-tight seals, e.g. between the end caps 16, 18, 19, 21 and connected fuel cells 10, 12, 16.

By electrically connecting the fuel cells 10, 12, 14 in the manner as known in the art (either in parallel or in series), and flowing fuel and oxidant through their respective flow paths, the stack 1 generates electricity by electrochemical reactions as known in the solid-oxide fuel cell art. The surfaces exposed to the flow of fuel are anodic, and may include catalytic material to promote the electrochemical reaction. The surfaces exposed to the flow of oxidant are cathodic.

The packaging of the fuel cells 10, 12, 14 provides a compact stack design that provides a higher energy production density than three similarly sized fuel cells arranged side-by-side, which would produce about the same power output but occupy more volume, and a single fuel cell which occupies the same volume but produces less power output. For example, for a fuel cell stack 1 with the outer fuel cell 14 having a diameter of 8mm, the middle fuel cell 12 having a diameter of 4mm and inner fuel cell 10 having a diameter of 2mm, and all fuel cells 10, 12, 14 having a length of 5 cm and producing 0.25W per cm^2, the stack 1 is expected to produce ~5.5W of power, and a corresponding energy density of ~2W/cm^3. In comparison, a single tubular fuel cell of diameter 8mm and 5 cm length and producing 0.25W per cm^2, will produce ~3.2W of power. Therefore, three fuel cell stack 1 produces nearly 70% more power while occupying the same volume as the single fuel cell.

With an outside diameter of between 4-10 mm and a power output of up to 10 W, the fuel cell stack 1 is expected to be suitable for use in small-size power applications, such as portable electronic devices. However, the improved power density provided by the compact packaging in the fuel cell stack 1 is expected to be also appreciated in larger-sized applications.

Referring back to Figures 1 and 2, an air diffuser 26 is provided at the bottom of the annular space between the inner and middle tubes 10, 12 to

distribute oxidant uniformly through this space. The diffuser 26 may be made of porous ceramics, cermet or metal.

Referring to Figure 3 and according to another embodiment of the invention, the fuel cell stack 1 as shown in Figures 1 and 2 is modified to include multiple oxidant supply conduits 20. As shown in Figure 3, four oxidant supply conduits 20 serve to feed oxidant into the stack 1, and a pair of oxidant exhaust conduit 22 serve to exhaust oxidant out of the stack 1. While four oxidant supply conduits 20 are shown in Figure 3, more supply conduits 20 may be added to increase the diffusion and uniform distribution of oxidant through the stack 1. The diffuser 26 may be omitted when a sufficient number of oxidant supply conduits 20 are provided to provide comparable oxidant diffusion and uniformity.

Referring to Figure 4 and according to another embodiment of the invention, the fuel cell stack 1 as shown in Figures 1 and 2 is modified to provide three inner fuel cells 10 arranged in a close-packed cluster. To fit within the middle fuel cell 12, the diameters of the inner fuel cells 10 are reduced so that the perimeter of the cluster is about the circumference of the inner fuel cell 10 shown in Figures 1 and 2. The cluster of inner fuel cells 10 provides a greater reactive surface area compared to the single inner fuel cell 10 shown in Figures 1 and 2, and as a result, the fuel cell stack 1 of this embodiment is expected to provide a higher power output than the fuel cell stack 1 as shown in Figures 1 and 2, when both stacks have similar exterior dimensions.

Multiple fuel cell stacks based on the embodiments described above and shown in Figures 1-4 may be assembled together to form a super-stack (not shown) to provide a greater power output than a single stack 1.

Referring to Figures 5 to 8 and according to another embodiment of the invention, a super-stack 30 may be formed of tubular SOFC fuel cells 32 assembled in rows and interspersed by metal plates 34. Each fuel cell 32 may

be a single fuel cell as described in Applicant's PCT application PCT/CA01/00634, or the fuel cell stack 1 as shown in Figures 1 to 4. The metal plates 34 include a metal base plate 38 coated with an oxidant-resistant coating 40 and a cathode coating 36. The metal plates 34 may be made of a metal suitable for high temperature SOFC operation such as Inconel, and serve as a support structure for the fuel cells 32, as well as a current collector. The oxidant resistant coating 40 may be for example, silver, gold, platinum, palladium, silver and Inconel alloy, silver and hastelloy, or an iron chromium alloy. The oxidant-resistant coating 40 serves to protect the base plate 38 from the high temperatures typically encountered during SOFC operation.

The metal plates may be substantially planar as shown in Figures 5, 7-8, or be corrugated as shown in Figure 6 to improve the support of each fuel cell 32. By establishing an electrical connection between the cathode layer 36 of the plate 34 and the cathode layers of the fuel cells 32, the electrical wiring (not shown) of the super-stack 30 may be simplified, by connecting wiring to the plates 34 instead of the cathode portion of each fuel cell 32.

Referring now to Figures 9 to 11, a fuel cell 48 is produced by EPD. Referring particularly to Figures 9(a) and (b), electrically conductive combustible cores 42 are arranged in a closely spaced pattern; the spacing is selected based on the wall thickness desired in the resulting stack 48. The cores 42 may be made of graphite, or any other conducting electrode that will combust during heat treatment. Then, as shown in Figures 10(a) and 10(b), electrode material is electrophoretically deposited on the cores 42 to form an inner electrode layer 44 which shape is defined by the geometric arrangement of the cores 42. After the inner electrode layer 44 has deposited and referring to Figures 11(a) and 11(b), electrolyte material is deposited on the electrode to form an electrolyte layer 46 which shape conforms to the geometry of the inner electrode layer 44. Then, a sintering heat treatment may be applied such that the cores 42 combust, leaving behind the inner electrode and electrolyte layers 44, 46. The fuel cell 48 may be

completed by applying an outer electrode layer (not shown) by known methods, such as dip-coating. The outer electrode layer may also be applied by EPD, in which case, before sintering, the outer electrode layer is applied to the electrolyte layer 36 by EPD.

By arranging the cores 42 in the pattern shown in Figures 9 to 11, a single fuel cell 48 having multiple first reactant flow paths (e.g. fuel flow path) is provided; such multiple first reactant flow paths provide a greater reactive surface area than a single first reactant flow path, and as a result, provide an increased power output. The cores 42 may be arranged in different patterns to produce a fuel cell 48 having different configurations, such as that shown in Figure 12.

While the present invention has been described herein by the preferred embodiments, it will be understood to those skilled in the art that various changes may be made and added to the invention. The changes and alternatives are considered within the spirit and scope of the present invention.

What is claimed is:

1. A solid oxide fuel cell stack comprising
   (a) a plurality of concentrically arranged tubular solid oxide fuel cells, each fuel cell having anode and cathode layers sandwiching an electrolyte layer, the plurality of fuel cells including an inner fuel cell and a second fuel cell around the outside of the inner fuel cell, the inner surface of the inner fuel cell and the outer surface of the second fuel cell both being one of the anode and cathode, and the outer surface of the inner fuel cell and the inner surface of the second fuel cell both being the other of the anode and cathode; and
   (b) top and bottom annular end caps each having an interior perimeter and an exterior perimeter, and each connected to opposite ends of the inner fuel cell around the interior perimeter, and to opposite ends of the second fuel cell around the exterior perimeter, the end caps, outer surface of the inner fuel cell and the inner surface of the second fuel cell defining an inner reactant chamber; and
   (c) an inlet to and an outlet from the inner reactant chamber for flow of a reactant therethrough;

   the anode and cathodes being electrically connectable to an external circuit such that electricity is produced by electrochemically reacting fuel and oxidant reactants, one reactant being fed through the inner fuel cell and over the outer surface of the second fuel cell, and the other reactant being fed through the inner reactant chamber.

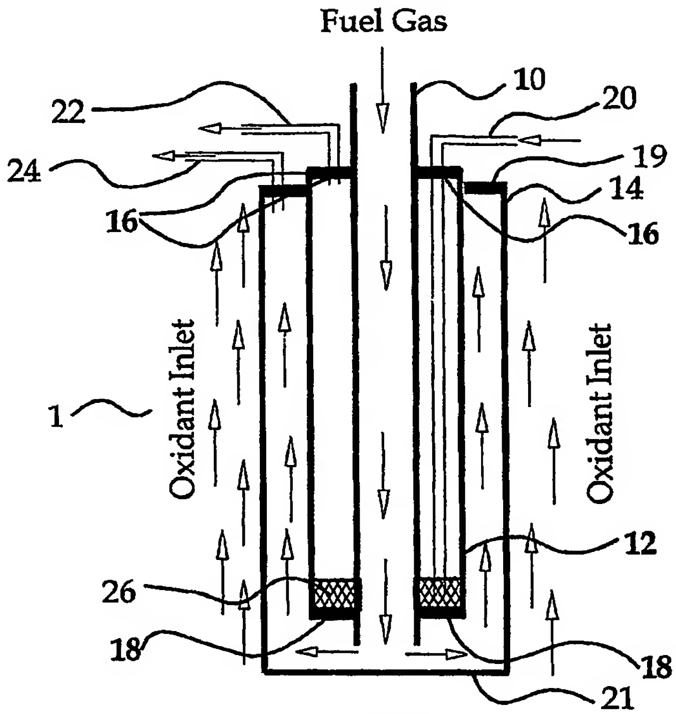
Fuel Gas
10
20
22
24
19
14
16
16
Oxidant Inlet
1
Oxidant Inlet
12
26
18
18
21

Fig.1

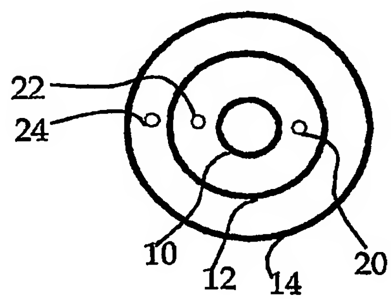
22
24
10
12
14
20

Fig.2

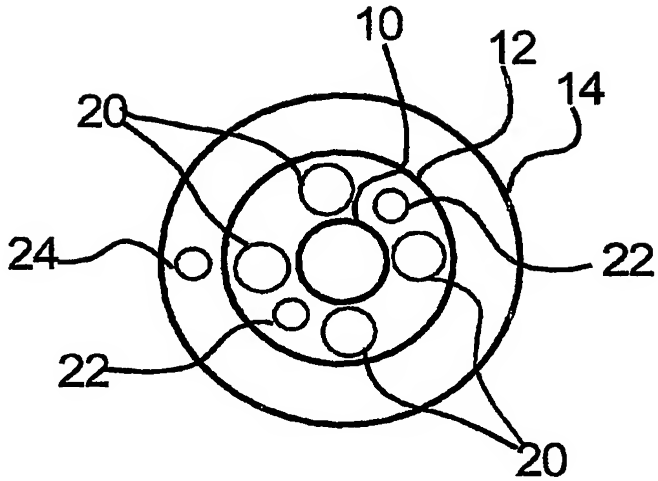

Fig.3

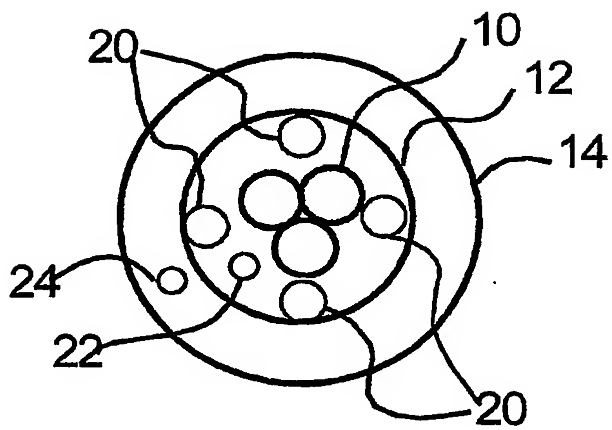

Fig.4

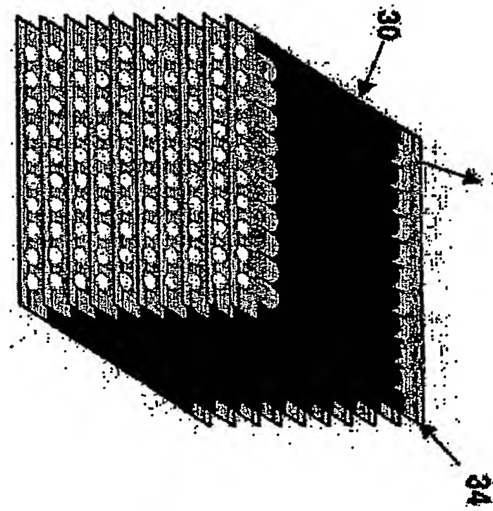

Fig. 5

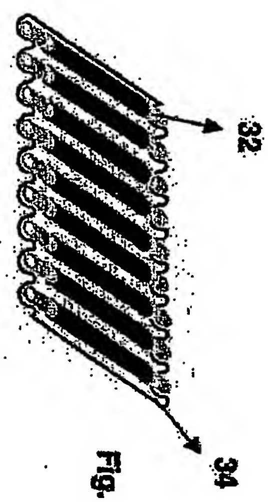

Fig. 6

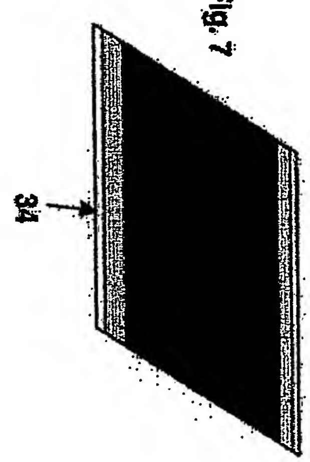

Fig. 7

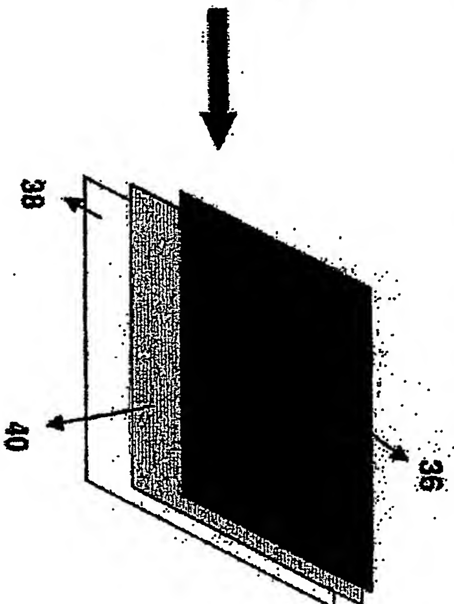

Fig. 8

Fig. 9(a)

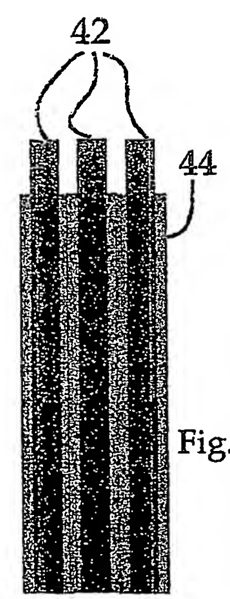

Fig. 10(a)

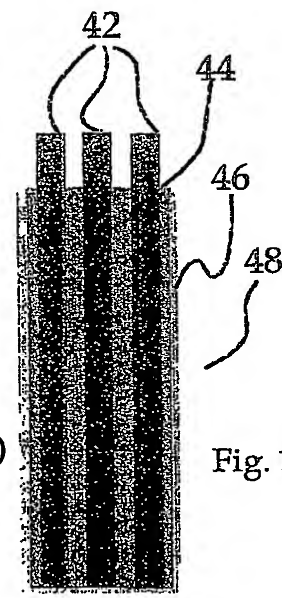

Fig. 11(a)

Fig. 9(b)

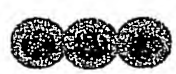

Fig. 10(b)

Fig. 11(b)

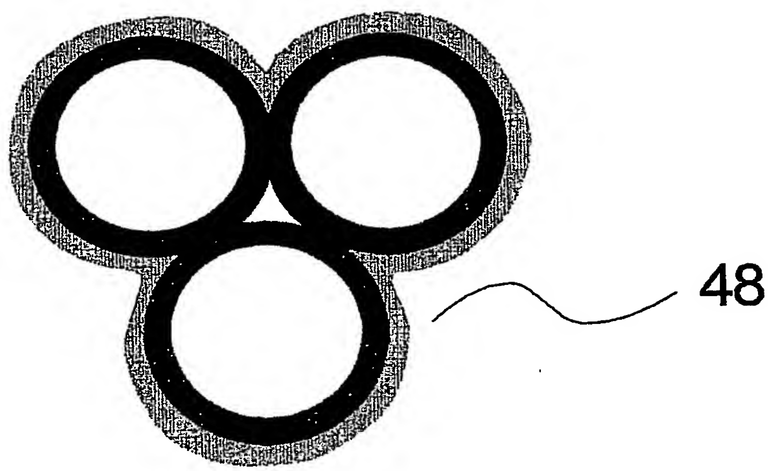

Fig.12